ARTICLE XI.

On the Neutral Sulphate of the Oxide of Ethyle, and the products of its decomposition by water.

By Charles M. Wetherill, Doctor of Philosophy. *Read July* 21, 1848.

The neutral sulphate of the oxide of Ethyle has, as is well known, been sought after for years in vain; the reason of which is, that it resembles in some of its properties the so called heavy oil of wine, and therefore a closer examination of it has been neglected. This body, however, is always formed when anhydrous sulphuric acid and anhydrous ether (or absolute alcohol) are brought together in the cold. The most convenient method of preparing it, is as follows:—A matrass containing pure ether is surrounded with a mixture of snow and salt, and by means of a retort, the neck of which is drawn out and bent at a right angle, anhydrous sulphuric acid is distilled into it, slowly, from Nordhausen oil of vitriol. It is not necessary to immerse the neck of the retort in the ether, as the acid fumes being heavy, fall, and slowly combine with it. A syrup-like liquid remains in the matrass, which is agitated with an equal volume of ether, and four times the volume of water. When the liquid has become divided into two strata, the ether, which contains the neutral sulphate in solution, is separated by a funnel from the other stratum, which is strongly acid, and contains sulphuric, sulphurous, æthionic, and sulphovinic acids, or if the temperature has not been kept sufficiently low, carbon, and together with the above named acids, isœthionic and methionic acids, resulting from the decomposition of æthionic acid. The ether solution is next agitated with milk of lime, to remove sulphurous acid, (this removes at the same time part of the colouring matter;) washed with water, filtered, and the ether distilled off.

An oily liquid remains in the retort, which contains a trace of ether, and is slightly acid. This acid reaction, I believe, is due to the water which was dissolved in the ether, and which, aided by the heat used in distilling off the ether, decomposes the compound. For if a portion of the ether in a watch glass be suffered to evaporate spontaneously, an oil remains which is perfectly neutral, but which quickly becomes acid when warmed with

a few drops of water. The oil is transferred from the retort to a capsule, well washed with a small quantity of water, the last portions of which are carefully removed with strips of paper, and placed in the vacuum over sulphuric acid to dry.

It is an oily liquid of pungent taste, leaving a burning sensation in the throat; a smell of peppermint oil; leaves an oily stain on paper, which disappears entirely—sp. gr. 1.120; colourless when pure, but as obtained above it is usually coloured yellow. It distils with the greatest difficulty, on which account I could not obtain a sufficient quantity of the distilled oil to analyze perfectly. In order to distil it the retort must be low in the neck, and a stream of carbonic acid passed through the liquid. At 100° the vapours rise in the form of exceedingly small globules, visible to the naked eye. At 110°, 120°, they pass over, when the heat is raised to 130°, 140°, the liquid blackens, sulphurous acid and alcohol pass over, and if heated above this, sulphurous acid and olefiant gas. The distillate is perfectly colourless, heavier than water, neutral to test paper, two combinations, one of the raw oil, another of the distilled, agreed, but the substance had not yet been freed from water over sulphuric acid in vacuo. Chlorine, in the cold, does not decompose it, but is dissolved, communicating to it a green colour: on adding water, the oil is precipitated.

Sulphuretted hydrogen in the cold has no effect upon it. A solution of caustic potash, saturated with sulphuretted hydrogen, changes it to mercaptan, and sulphate of potash, unaccompanied by any other oil, as was proved by absorbing the mercaptan by oxide of mercury; the reaction appears to be $C_4H_5O, SO_3 + KSHS = C_4H_5S, HS + KO, SO_3$. The neutral sulphate is soluble in fuming nitric acid, from which it is precipitated by water. If caustic potash be now added till the liquid is nearly neutral, and the whole heated, hyponitrite of ethyle ($C_4H_5ONO_3$) is formed. This reaction was anticipated, as nitrate of potash, sulphuric acid, and alcohol, give the hyponitrite. Treated in the same way with HCl and KOHO, an oil distils over, heavier than water, having a smell of apples. With potassium, in the cold, it is unchanged; when warmed, the potassium takes fire, and among the other products, mercaptan is formed. With water, in the cold, after a lapse of time, when heated quickly, the oil disappears entirely, leaving a very acid solution. In vacuo it does not become green like the oil of wine described by Serullas.

The neutral sulphate of the oxide of ethyle, or, in short, sulphuric ether, has never been analyzed. Liebig made a single combustion of the oil, from sulphuric acid and alcohol, (which is probably identical with this.) The combustion was made merely for the purpose of trying his new method of organic analysis upon liquids slightly volatile. He did not make a sulphur determination. His results are as follows: 1.730 substance gave $CO_2 = 2.078$; $C = 33.485\%$ $HO = 0.940$ $H = 6.150\%$; which results agree with Serullas' formula for the heavy oil of wine. But at the same time he notices, without attempting to account for it, an essential difference from Serullas' oil, namely, that warmed with water, it did not give an oil free from sulphuric acid, but entirely disappeared.

The oil analyzed had a slight trace of acid, was freed from water by standing for several days over sulphuric acid in vacuo. The combustion was made in the ordinary way, the liquid being placed in a small closed tube, which was dropped into the combustion tube and the oil suffered to run out upon the sides. The results are as follows:

	Grammes.					
No. 1, with Cu O—	0.853,	gave $CO_2 = 0.960$;	$C = 30.692\%$*	and $HO = 0.484$;	$H = 6.307\%$.
No. 2, with $PbO\,CrO_3$	0.7905,	" " $= 0.8845$;	$C = 30.511\%$	" $= 0.450$;	$H = 6.325\%$.
No. 3, with CuO & $KO\,ClO_5$,	0.7530,	" " $= 0.849$;	$C = 30.743\%$	" $= 0.4251$;	$H = 6.268\%$.

The sulphuric acid was determined by heating the substance, till it disappeared, in a small retort containing caustic potash: to the neck of the retort was adapted a tube which was kept cool with wet paper, to prevent any of the oil escaping. The potash solution was transferred to a silver capsule, evaporated to dryness and strongly ignited;—redissolved in water, neutralized with hydrochloric acid, and the sulphuric acid precipitated by chloride of barium. These are the results of three experiments:

	Grammes.		
No. 1,	0.4895	gave Ba. $OSO_3 = 0.7372$;	$SO_3 = 51.559\%$.
No. 2,	0.4314	" " $= 0.6485$;	" $= 51.553\%$.
No. 3,	0.439	" " $= 0.6652$;	" $= 51.950\%$.

The mean of these six analyses compared with the calculation of the formula $C_4 H_5 O\,SO_3$ is as follows:

		Calculated.		Experiment.
C_4	— 300	31.169	—	30.648
H_5	— 62.5	6.494	—	6.300
O	— 100	10.389	—	11.365
SO_3	— 500	51.948	—	51.687
	962.5	100.000		100.000

The heavy oil of wine, calculated, gives the following numbers:

		Calculated.
C_6	— 600	— 33.103
H_9	— 112.5	— 6.207
O	— 100	— 5.517
$2\,SO_3$	— 1000	— 55.173
	1812.5	100.000

The products of the decomposition of the neutral sulphate of the oxide of ethyle by water.

When water is added to sulphate of ether, the mixture heated, and from time to time shaken, the oil entirely disappears, leaving a very acid solution, which, when heated, gives off alcohol. If carbonate of barytes be added, until the liquid is saturated, three salts of barytes remain in solution. The filtered solution evaporated by a gentle heat, deposits a small quantity of crystals in the form of scales, before it is well concentrated. Spirits of wine is now added, which precipitates the remainder of this salt. Redissolved in water and precipitated by alcohol, it is obtained in fine white scales, which, when dried, have a pearly lustre. This salt has the characteristics of methionate of barytes, with which it corresponds in composition. 0.4025 of the salt, dried at 100°, ignited with $SO_3\,HO$, gave

* Per centage.

0.271 Ba O S O_3, which corresponds to 44.248%, Ba O 0.544 burned with chromate of lead, gave C O_2 = 0.0555; C = 2.776% & H O = 0.095; H = 1.930%.

		Calculated.	Experiment.
Ba O	—	44.033	44.248
C	—	3.517	2.776
H_2	—	1.722	1.930
O_7	—	—	—
S_2	—	—	—

The mother liquid of these crystals contains a salt soluble in alcohol, and which, purified by several crystallizations from spirits of wine, is obtained in fine needles. This salt is a mixture of sulphovinate with isœthionate of barytes. These two salts, when dried over sulphuric acid in vacuo, have exactly the same composition. The substance used for analysis contained a trace of alcohol, which was difficult to get rid of over sulphuric acid.

Ignited with sulphuric acid,

No. 1, 0.376 gave Ba O S O_3 = 0.219; Ba O = 38.271%.
No. 2, 0.443 " " = 0.258; " = 38.262%.

No. 1, 0.621 burned with chromate of lead, gave C O_2 = 0.296; C = 12.995% & H O = 0.1725; H = 3.075%.

		Calculated.	Found.
Ba O	—	39.579	38.271
C_4	—	12.392	12.995
H_5	—	2.582	3.075
O	—	—	—
2 SO_3	—	—	—

The salt analyzed was half sulphovinate, half isœthionate of barytes, as is shown by the following experiment. Sulphovinic acid, as is well known, is resolved at the boiling temperature into sulphuric acid and alcohol. Isœthionic acid is unchanged at the same temperature. 4.504 grammes of the salt, dissolved in water, and the barytes precipitated by sulphuric acid, gave Ba O S O_3 = 2.6005 or Ba O = 37.877%. The filtered solution boiled for several hours, saturated with carbonate of barytes, and the soluble isœthionate of barytes, precipitated by sulphuric acid, gave Ba O S O_3 = 1.105, whence Ba O = 16.776% of the original salt. But the acids before boiling saturated 37.877% of barytes, or nearly twice as much. The substance is therefore a mixture half sulphovinate, half isœthionate of barytes.

As the heavy oil of wine is not one of the products in the action of anhydrous sulphuric acid upon anhydrous ether, the explanation heretofore given of this reaction is necessarily erroneous. In the case of alcohol, the anhydrous acid was said first to form hydrated bisulphate of the oxide of ethyle, an excess of the acid decomposes the combined oxide of ethyle, depriving it of the elements of water, forming heavy oil of wine, and at the same time setting free the substance $C_4 H_4$, which combining with 4 SO_3 & H O, form ethionic acid.

In the case of ether, the sulphuric acid was said to extract the elements of water, form-

ing heavy oil of wine; the hydrated acid unites with the ether to form bisulphate of the oxide of ethyle, and by the farther action of the anhydrous sulphuric acid, the same reaction takes place as in the case of alcohol.

Not the slightest trace, however, of heavy oil of wine is to be detected in the substance resulting from the action of anhydrous sulphuric acid upon ether and alcohol. Portions of this oil, obtained from ether and from alcohol, were decomposed by water, distilled, and the distillate suffered to stand several days over chloride of calcium; the experiment in the case of ether was repeated several times, but not the slightest indication of a light oil of wine was to be detected.

The following may possibly be the reaction which takes place. The anhydrous sulphuric acid partly unites with the oxide of ethyle to form the neutral compound, ($C_4 H_5 O S O_3$,) and partly decomposes the ether, taking from it water to form Regnault's compound ($4 S O_3 C_4 H_4$,) which unites with one equivalent of water to form æthionic acid, ($4 S O_3 C_4 H_5 O$.) Another portion of the sulphuric acid takes water and unites with ether to form sulphovinic acid.

In the case of alcohol; part of the sulphuric acid takes water from the alcohol to form hydrated acid, which, with another portion of alcohol, forms hydrated sulphovinic acid; the ether thus set free, partly combines with the sulphuric acid to the neutral sulphate; partly is decomposed, as in the case of ether, to æthionic acid.

The decomposition products of the heavy oil of wine, by water are sulphovinic acid, and a carburetted hydrogen, the so called light oil of wine. The decomposition products of sulphate of ether by water, are materially different, being isœthionic and sulphovinic acids, with methionic acid in small quantity, evidently an after product.

4 equivalents of the neutral sulphate, with 3 eq. water, give 1 eq. isœthionic acid, 1 eq. sulphovinic acid, and 2 eq. alcohol,—thus

$$4 (S O_3, C_4 H_5 O) + 4 H O = 2 S O_3, C_4 H_6 O_2 + 2 S O_3, C_4 H_5 O, H O + 2 (C_4 H_5 O, H O.)$$

According to Regnault, the corresponding neutral sulphate in the methylic series, is formed in a similar manner, by the action of anhydrous sulphuric acid upon methylic ether. I performed the above experiments while under the instruction of Professor Liebig, to whom I express my kindest thanks.

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